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**FAILURE CRITERIA FOR POLYMERIC SOLIDS**

BY

**L. NICOLAIS AND A. T. DIBENEDETTO**

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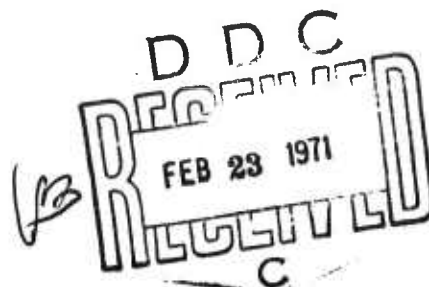
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JANUARY 1971

MONSANTO/WASHINGTON UNIVERSITY ASSOCIATION  
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## FOREWORD

The research reported herein was conducted by the staff of the Monsanto/Washington University Association under the sponsorship of the Advanced Research Projects Agency, Department of Defense, through a contract with the Office of Naval Research, N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 876, ONR contract authority NR 356-484/4-13-66, entitled "Development of High Performance Composites."

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## FAILURE CRITERIA FOR POLYMERIC SOLIDS

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### ABSTRACT

A theory for predicting the stress-strain characteristics of polymeric solids is developed in terms of a description of microdefect formation. The process of irreversible change in these solids is assumed to be a combination of nucleation of sub-microscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. Straining results in the simultaneous generation of free volume and macrodefects so that catastrophic failure can occur through either a general yielding of the material or by brittle fracture.

It is assumed that nucleation of sub-microscopic defects is an activated process and that defect growth is one dimensional and linear. The total strain is expressed as the sum of an elastic recoverable strain and a nonlinear, nonrecoverable strain and expressions are obtained for the stress as a function of time,

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\*On leave from the Laboratorio di Ricerca su Tecnologia dei Polimeri e Reologia del C.N.R. Napoli, Italy.

temperature and loading history. The criterion for yielding is defined in terms of free volume concepts and a criterion for brittle failure is defined in terms of a critical defect size. The parameters of the resulting model are calculated for polyphenylene oxide polymers based on constant rate of loading experiments and then the general creep behavior, including the time required under constant load for cold flow, is predicted. Experimental data are shown to agree with these predictions.

## FAILURE CRITERIA FOR POLYMERIC SOLIDS

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### Introduction

At temperatures well below the primary glass transition, most organic polymers exhibit either brittle or ductile failure, depending upon the load and temperature history imposed on the material. When ductile, these polymers are tough and resistant to impact and when brittle they are not. Polyblending with finely dispersed rubber particles often results in large increases in toughness, while polyblending with coarse rigid particles often results in increased brittleness.

The difficulty in describing the stress-strain behavior is complicated by many factors, of which the formation and growth of defects during loading is perhaps the most important. It is well known that the presence of stress inhomogeneities and/or finely dispersed second phases can induce crazes, cold flow and a multitude of interacting cracks. It is the purpose of this paper to offer a rational theory to describe the stress-strain behavior of glassy polymeric solids.

### Theory

The process of irreversible change in a polymeric solid is assumed to be a combination of nucleation of sub-microscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. These defects might be either true cracks,



in which case continued straining of the material results in the generation of a volume change in the solid (1) or they might be crazes, in which case continued straining of the material results in the generation of free volume (2-4). In any case, they lead to catastrophic failure through either a general yielding of the material or a brittle fracture.

In developing any theory of failure it is necessary to set criteria for both types of failure and then predict which will occur first under a given set of loading conditions.

In this paper we deal specifically with amorphous polymeric solids which tend to craze under the influence of an external load. It has been observed that under a unidirectional tensile load crazes will nucleate and grow perpendicular to the direction of loading. Under certain conditions they tend to overlap and coalesce to form a nearly continuous zone of crazed material which ultimately leads to a general cold drawing, or macroscopic yielding, of the solid. This condition can be observed experimentally by the development of necking and optical birefringence in the solid, or less precisely, by the appearance of an apparent maximum in the engineering stress-strain curve. Under certain conditions, these crazes can grow to a greater length than can be tolerated by the material and the craze rapidly changes to a macroscopic crack which propagates catastrophically, causing failure in a brittle manner.

It is assumed that the nucleation of craze sites is an activated process. Based on the work of Zhurkov et al. (5),

one can empirically justify the following form for the initial nucleation rate:

$$\frac{dN}{dt} = N_0 \left( \exp - \frac{\Delta E_N}{RT} \right) \sinh \left( \frac{(n-1)\sigma}{\sigma^*} \right) \quad (1)$$

where  $N_0$  is a constant,  $\Delta E_N$  is an activation energy and  $\sigma^*/(n-1)$  is a characteristic stress constant. For very long term loading Zhurkov's data show that it is necessary to account for an exponential decrease in the nucleation rate using a decay factor  $\exp - t/\lambda(\sigma, T)$ . However, Equation (1) is satisfactory for short term stress-strain behavior.

Once craze sites have been nucleated, their growth can be represented by a one dimensional, linear growth process (6). It is assumed that the growth rate  $\frac{dG}{dt}$  is given by:

$$\frac{dG}{dt} = G_0 \left( \exp - \frac{\Delta E_G}{RT} \right) \sinh \frac{\sigma}{\sigma^*} \quad (2)$$

where  $G_0$  is a constant,  $\Delta E_G$  an activation energy and  $\sigma^*$  a characteristic stress constant.

The isothermal rate of formation of craze volume  $\left( \frac{dv_f}{dt} \right)_T$  can then be obtained from the product of nucleation and growth rates as:

$$\begin{aligned} \left( \frac{dv_f}{dt} \right)_T &= \beta_0 N(t) \frac{dG}{dt} \\ &= B(T) \sinh \frac{\sigma}{\sigma^*} \int_0^t \sinh \frac{(n-1)\sigma}{\sigma^*} dt \end{aligned} \quad (3)$$

$$\text{where } B(T) = \beta_0 N_0 G_0 \exp - \frac{(\Delta E_N + \Delta E_G)}{RT} \quad (4)$$

and  $\beta_0$  is a proportionality constant.

In the glassy state, one can neglect pure viscous flow and following the suggestion of DiBenedetto and Trachte (7), the total strain can be expressed as the sum of two terms, a linear elastic (and recoverable) strain and a non-linear (and irrecoverable) strain. The elastic strain is equated to the initial elasticity of the material  $\sigma/E_S$  and the irrecoverable strain is equated to the strain caused by the additional craze volume:

$$\begin{aligned} \epsilon &= \epsilon_S + \epsilon_C \\ &= \frac{\sigma}{E_S} + \frac{V_f(t)}{(1-2\mu)} \end{aligned} \quad (5)$$

where  $\sigma$  is the stress,  $E_S$  the initial elastic modulus,  $\mu$  the Poisson ratio and  $V_f(t)$  the craze volume obtained from integration of equation (3).

Equation (5) gives the relationship between stress, strain, temperature and time. In order to fix a point of failure for the material, failure criteria must be established. It is assumed, in accordance with free volume concepts (2,3), that the criterion for yielding, or the onset of cold flow,

is given by:

$$V_f(t_y) = (\Delta\alpha) (T_m - T) \quad (6)$$

where  $(\Delta\alpha)$  is a constant related to the difference in thermal expansion coefficients of the glassy and fluid states and  $T_m$  is the maximum temperature at which craze sites can nucleate. The temperature  $T_m$  has been related to the glass temperature  $T_g$  (7) and sometimes is considered to be slightly higher than  $T_g$  (8). In this paper it is left as a measurable parameter.

It is also assumed that the criterion for brittle failure is determined by a critical flaw length  $l_C^*(T, \rho_C)$  that is primarily a function of temperature and flaw density.

Thus, whether the material yields before brittle fracture depends upon whether the formation of crazes develops sufficient free volume  $V_f(t_y)$  before reaching a critical flaw size  $l_C^*$ . Which criterion is reached first, depends upon the relative rates of nucleation and growth. The stress-strain behavior under some well-defined loading conditions will be considered next.

#### A. Creep

In a creep experiment the stress is constant at  $\sigma_0$ . The integration of equation (3) and substitution of  $V_f(t)$  into equation (5) gives:

$$\epsilon_t = \frac{\sigma_o}{E_S} + \frac{B(T)}{2(1-2\mu)} \left( \sinh \frac{n\sigma_o}{\sigma^*} \right) t^2 \quad (7)$$

The first term on the right side of equation (7) represents the recoverable elastic deformation and the second term the irrecoverable deformation associated with craze formation. The use of equation (6) for the yield criterion leads to the following expression for the time to yield  $t_y$  (i.e., the time required to initiate cold drawing)

$$t_y = \left\{ \frac{2(\Delta\alpha)(T_m - T)}{B(T) \sinh \frac{n\sigma_o}{\sigma^*}} \right\}^{\frac{1}{2}} \quad (8)$$

Integration of equation (2) gives the defect size at the yield point  $G(t_y)$  as:

$$G(t_y) = G_o \left( \exp - \frac{\Delta E_G}{RT} \right) \left( \sinh \frac{\sigma_o}{\sigma^*} \right) \quad (9)$$

If  $G(t_y) \geq \ell_C^*$  brittle failure occurs before cold drawing.

#### B. Constant Loading Rate

In this case the stress is a linear function of time,  $\sigma = E_S r_o t$ , and the rate of loading  $\dot{\sigma}$  is constant and equal to  $E_S r_o$ . The integration of equation (3) gives:

$$V_f = \frac{B(T)\sigma^{*2}}{(n-1)\dot{\sigma}^2} \left[ \frac{\cosh \frac{n\sigma}{\sigma^*}}{2n} + \frac{\cosh \frac{(2-n)\sigma}{\sigma^*}}{2(2-n)} - \cosh \frac{\sigma}{\sigma^*} - \frac{1}{n(2-n)} + 1 \right] \quad (10)$$

From experimental observation it is found that  $n > 1$  and  $\sigma_y/\sigma^* \gg 1$  so that for all practical purposes over most of

the stress-strain curve, equation 10 reduces to:

$$V_f = \frac{B(T) \sigma^{*2}}{4 \dot{\sigma}^2 n(n-1)} \exp \frac{n\sigma}{\sigma^*} \quad (11)$$

Substitution of equation (11) into equation (5) gives:

$$\epsilon_t(\sigma) = \frac{\sigma}{E_S} + \frac{B(T) \sigma^{*2} (\exp \frac{n\sigma}{\sigma^*})}{4 \dot{\sigma}^2 n(n-1) (1-2\mu)} \quad (12)$$

Since the criterion for yielding is  $V_f(\sigma_y) = (\Delta\alpha)(T_m - T)$ , the yield stress can be obtained from equation (11) as:

$$\exp \frac{n\sigma_y}{\sigma^*} = \left[ \frac{4 \Delta\alpha (T_m - T) n(n-1)}{B(T) \sigma^{*2}} \right] \dot{\sigma}^2 \quad (13)$$

The sensitivity of yield stress to loading rate is given by:

$$\frac{d\sigma_y}{d \ln \dot{\sigma}} = \frac{2\sigma^*}{n} \quad (14)$$

which predicts that yield stress is a linear function of rate of loading. The temperature dependence of yield stress is given by:

$$\frac{d\sigma_y}{dT} = - \frac{\sigma^*}{n} \left[ \frac{(\Delta E_N - \Delta E_G)}{RT^2} + \frac{1}{(T_m - T)} \right] \quad (15)$$

which shows that the temperature dependence of yield stress is controlled primarily by the difference in activation energies between the nucleation and growth processes.

The defect size at the yield point can be obtained from integration of equation (2):

$$G(\sigma_y) = G_0 \exp - \frac{\Delta E_G}{RT} \left[ \frac{2^{2-n} (\Delta\alpha) (T_m - T) n (n-1)}{B(T) \sigma^* 2^{-n}} \right]^{1/n} \dot{\sigma}^{\frac{2-n}{2}} \quad (16)$$

### C. Constant Strain Rate

The major difficulty in analyzing constant strain rate data is that the rate of formation of craze volume is defined as an integral of stress over time (equation 3) and since the stress-strain curve is non-linear, the dependence of stress on time is not known. One can, however, define the stress-strain relation as  $\sigma = E_S(\sigma) (r_0 t)$  where  $E_S(\sigma)$  is a stress dependent modulus and  $r_0$  is the rate of straining. From observation of experimental stress-strain curves, a reasonable expression for the time dependence of the stress to nearly the yield point is:

$$\frac{d\sigma}{dt} \doteq E_{S0} r_0 \exp - \frac{\delta \sigma}{\sigma^*} \quad (17)$$

where  $\delta$  is a constant of the order of 0.01 to 0.1. The use of equation (17) in equation (3) leads to

$$V_f \doteq \frac{B(T) \sigma^{*2} \exp \frac{(n+2\delta) \sigma}{\sigma^*}}{4 E_{S0}^2 r_0^2 (n+\delta-1) (n-2\delta)} \quad (18)$$

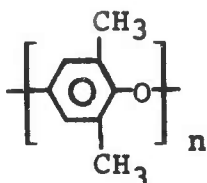
and

$$\frac{d\sigma_y}{d \ln r_0} \doteq \frac{2\sigma^*}{n+2\delta} \quad (19)$$

As long as the stress-strain curve is nearly linear, constant rate of loading and constant rate of straining result in nearly the same behavior with the yield stress being slightly less dependent on strain rate than on stress rate.

### Experimental Results

The material studied was General Electric's Grade 631-111 polyphenylene oxide with a glass transition temperature of  $T_g = 210^\circ\text{C}$ , a Poisson's ratio of 0.35 and a structural formula:



Test specimens were compression molded at  $285^\circ\text{C}$  followed by a slow cooling to room temperature. All samples were annealed below  $T_g$  to minimize molding stresses. Standard ASTM tensile tests were carried out on a modified Instron Testing machine which could be controlled for both constant load and constant rate of loading as well as constant rate of deformation. Tests were conducted at temperatures ranging from  $25^\circ\text{C}$  to  $200^\circ\text{C}$  and at strain rates ranging from 0.00526 to 0.526 in/in-min.

A typical stress-strain curve is shown in Figure 1. The yield point was assumed to be the maximum in the curve. If failure occurred before this maximum, it was defined as brittle failure. The elastic strain was measured from the initial elastic modulus and the irrecoverable deformation was associated with the non-linear portion of the stress-strain curve. A summary of the yield stress data at constant loading rate and constant deformation rate over a range of temperatures is given in Figure 2. Time-temperature superpositioning at a



reference temperature of 34°C (9) was used to condense the data and the required shift factor  $a_T$  is given by:

$$\log_{10} a_T = \frac{8,750}{T} - 28.0$$

where T is the temperature in degrees Kelvin.

The effect of temperature on yield stress is shown in Figure 3. According to the yield criterion (equation 6), the irreversible strain at the yield point should be a linear function of temperature and independent of loading rate. Table 1 shows that it was independent of loading rate and its temperature dependence can be expressed as:

$$(\epsilon_p)_y = V(t_y)(1-2\mu) = 3.09 \times 10^{-5} (525-T)$$

in agreement with theory. Figure 4 illustrates the appearance of the crazes for a variety of test conditions. An average defect size was measured from such pictures and the results are shown in Figure 5. Defect size is seen to be a complex function of strain rate and temperature. As long as the defect size was below the locus of points representing  $l_C^*$ , the failure was by yielding, while if the defect size was greater than  $l_C^*$  the failure was brittle. It is reasonable to expect that the critical crack size is a function of temperature, defect density and defect size distribution so that it is probably more realistic to imagine a narrow zone about the locus of points representing  $l_C^*$  which divides the brittle and ductile zones.

From the data shown in Figures 2 to 5 and using equations 4 and 12 to 16, one may evaluate all of the constants required to define the stress-strain behavior of the material. These values are listed below:

$$\Delta\alpha = 3.09 \times 10^{-5} \text{ } ^\circ\text{K}^{-1}$$

$$T_m = 525^\circ\text{K}$$

$$\sigma^* = 334 \text{ psi}$$

$$n = 2.3$$

$$\Delta E_N = 41,700 \text{ cal/g-mole}$$

$$\Delta E_G = 32,300 \text{ cal/g-mole}$$

$$\beta_O G_O N_O = 2 \times 10^{20} \pm 100\%$$

The values for the activation energies are reasonable for the assumed processes and the value of  $\sigma^*$  is very low compared to the yield stresses in the material. Because of this latter fact the constant  $\beta_O G_O N_O$  is susceptible to large error. The limits of  $\pm 100\%$  in  $\beta_O G_O N_O$  correspond to a  $\pm 100$  psi error in load measurement or a  $\pm 1^\circ\text{C}$  in temperature control.

The primary value of such a model is to predict the mechanical behavior in other modes of loading, based on the data from constant loading rate experiments. By using equations (7) to (9), one can calculate the irreversible deformation, the time to yield and the defect size at the yield point under a constant load. Creep-recovery experiments were run in order to experimentally determine these quantities. The theoretical curves and the experimental data are

shown in Figures 6 to 8. The irrecoverable deformation as a function of time was calculated from the second term on the right hand side of equation (7). The experimental values shown on Figure 6 agreed with theory to within experimental accuracy. Similarly, the experimental values for time to yield agreed with those calculated from equation (8), as shown in Figure 7. When the failure was in the brittle mode, it occurred earlier than the calculated value for yield time. These points are marked by the symbol B in Figure 7. Equation 9 is used to calculate average defect size at yield and the theoretical curves are plotted in Figure 8. The values of  $l_C^*$  shown in Figure 8 were obtained from Figure 5. As predicted, when the defect size was above  $l_C^*$  a brittle failure was encountered. When ductile failure was attained, the calculated values of defect size agreed with experiment.

#### Concluding Remarks

A theory for predicting the stress-strain characteristics of polymeric solids has been presented. The process of irreversible change is assumed to be a combination of nucleation of submicroscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. The total strain is expressed as the sum of an elastic recoverable strain and a non-linear non-recoverable strain and expressions are

obtained for the stress as a function of time, temperature and loading history. The criterion for yielding is defined in terms of free volume concepts and a criterion for brittle failure is defined in terms of a critical defect size.

It has been shown that the resulting model quantitatively describes the mechanical behavior of polyphenylene oxide and that by using stress-strain data obtained at constant rate of loading, one can predict the creep behavior of the material at constant load. A description of the ductile-brittle transition has also been presented and it has been shown that one can qualitatively define the locus of points separating the ductile from the brittle behavior.

Concerning this latter point, it is well known that brittle failure is a stochastic process and that one cannot predict with absolute certainty the time for brittle failure. This implies that the brittle-ductile transition cannot be represented by a single locus of points, but rather the two regions are separated by a narrow transition zone within which both modes of failure are more or less equally probable. A second point is that the concept of a simple critical crack dimension for brittle failure is oversimplified and the criterion for brittle failure must certainly be examined in terms of stress intensity factors. Both of these points are presently under study.

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Table 1. The Irrecoverable Strain at Yield,  $\epsilon_p = V_f(T_Y)/(1-2\mu)$   
as a Function of Temperature and Strain Rate.

$\epsilon_p \times 10^2$  in/in

$\dot{\epsilon}$ T°C	2.62 $\times 10^{-3}$	5.24 $\times 10^{-3}$	1.31 $\times 10^{-2}$	2.62 $\times 10^{-2}$	5.24 $\times 10^{-2}$	1.31 $\times 10^{-1}$	2.62 $\times 10^{-1}$	5.24 $\times 10^{-1}$	1.31
34	2.12	2.00	2.20	2.20	2.28	2.28		2.30	2.38
52		2.08		2.18		2.12		2.12	
63	1.78	1.80	1.75	1.91	1.90	2.00	1.95	2.00	2.08
81		1.65		1.80		1.72		1.75	
100		1.40	1.43	1.57	1.53	1.55	1.68	1.68	1.60
115		1.35		1.40		1.35		1.52	
130	1.30	1.10		1.18	1.20	1.22	1.35	1.25	
140		1.18		1.15		1.13		1.22	

$\dot{\epsilon}$  in/in-min

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- Figure 7. Time to yield under constant load.
- Figure 8. The effect of creep stress on the average defect size.



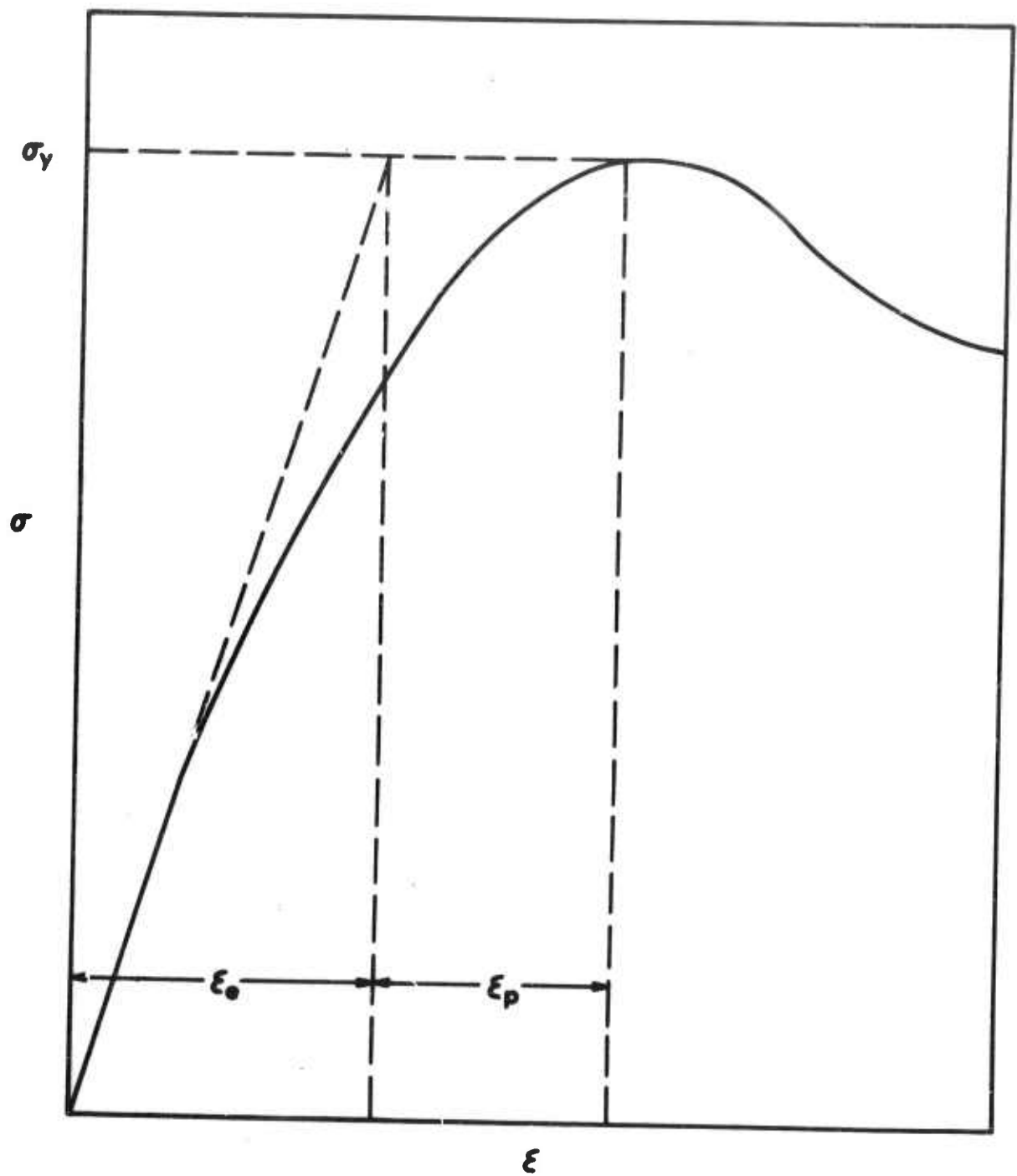


Figure 1. A typical engineering stress-strain curve for PPO.

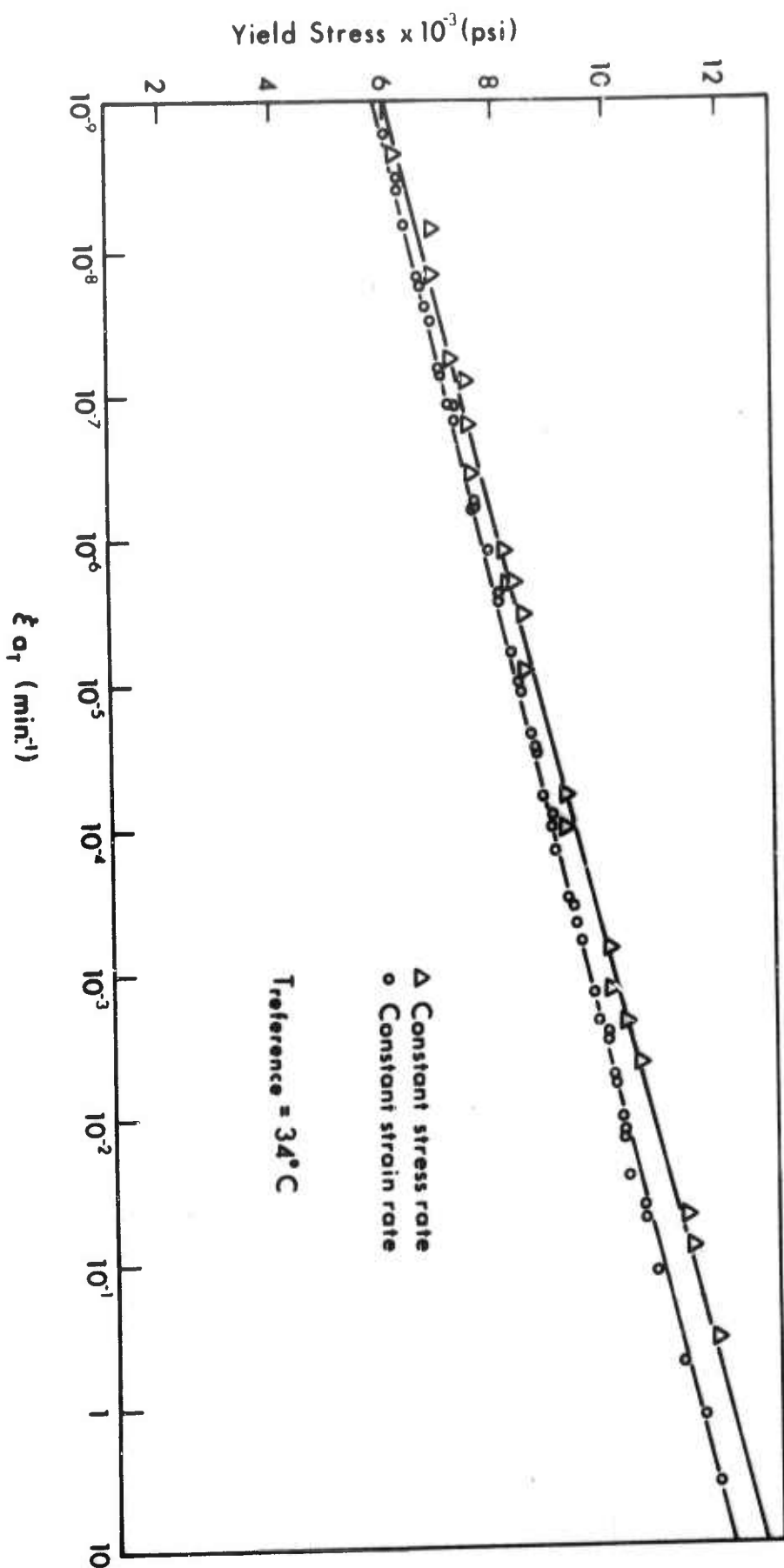


Figure 2. Effect of strain rate on yield stress.

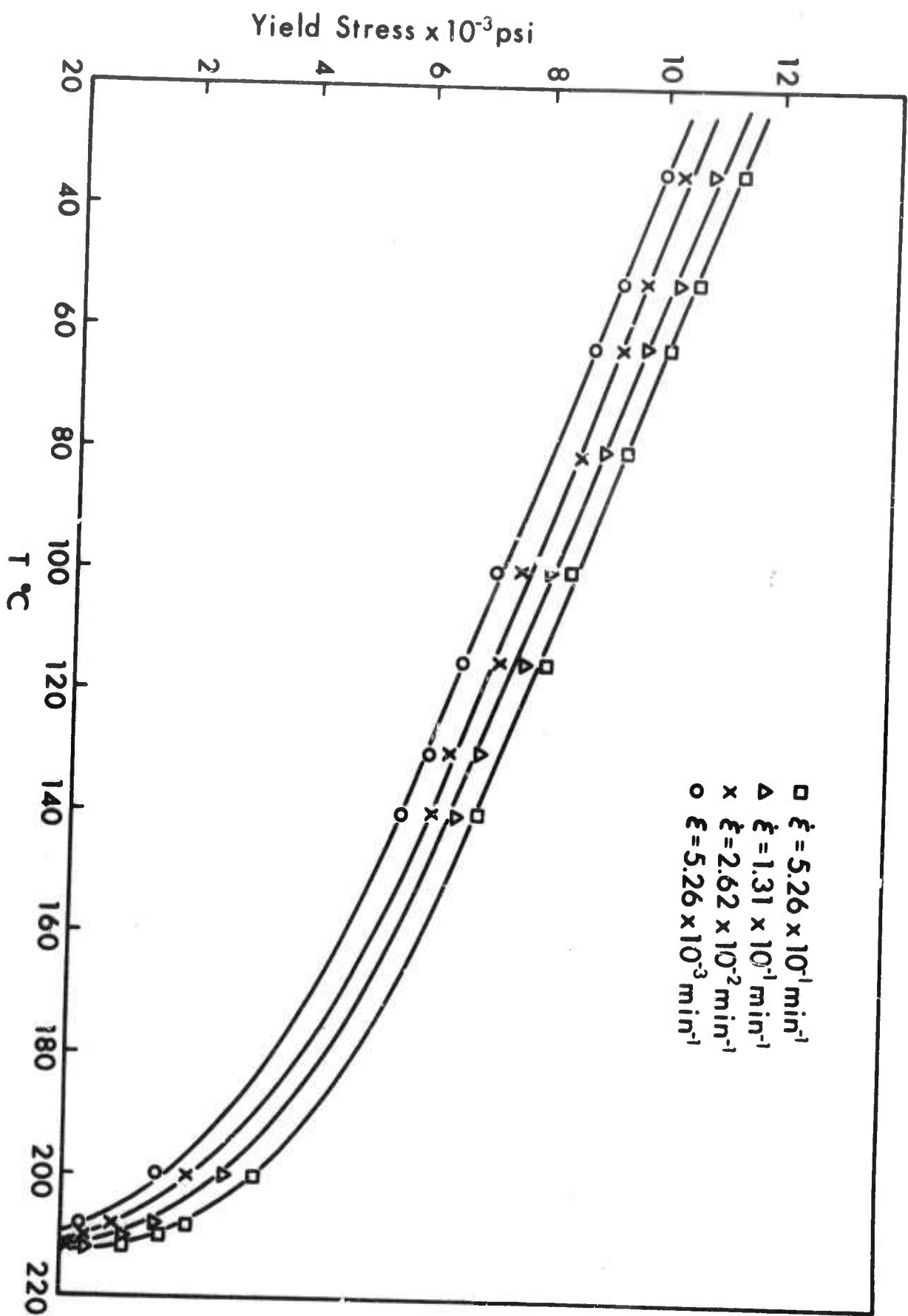
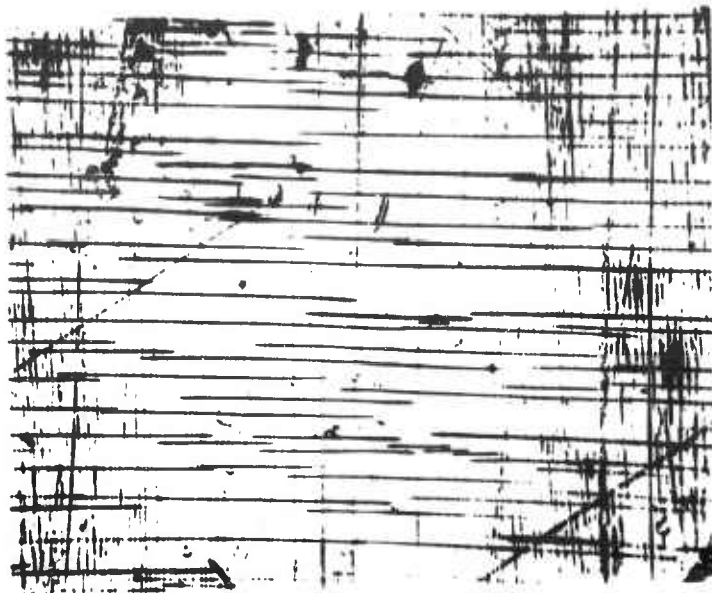
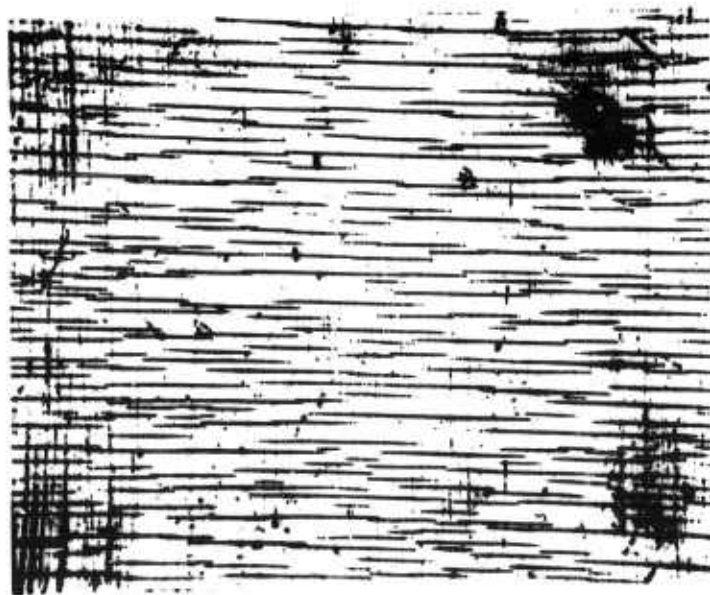


Figure 3. Effect of temperature on yield stress.



10.2mm.

$\sigma_0 = 3600 \text{ psi}$   $T = 140^\circ \text{C}$   $t = 3 \text{ min.}$



10.2mm.

$\sigma_0 = 3600 \text{ psi}$   $T = 172^\circ \text{C}$   $t = 3 \text{ min.}$

Figure 4. Illustration of the appearances of crazes.

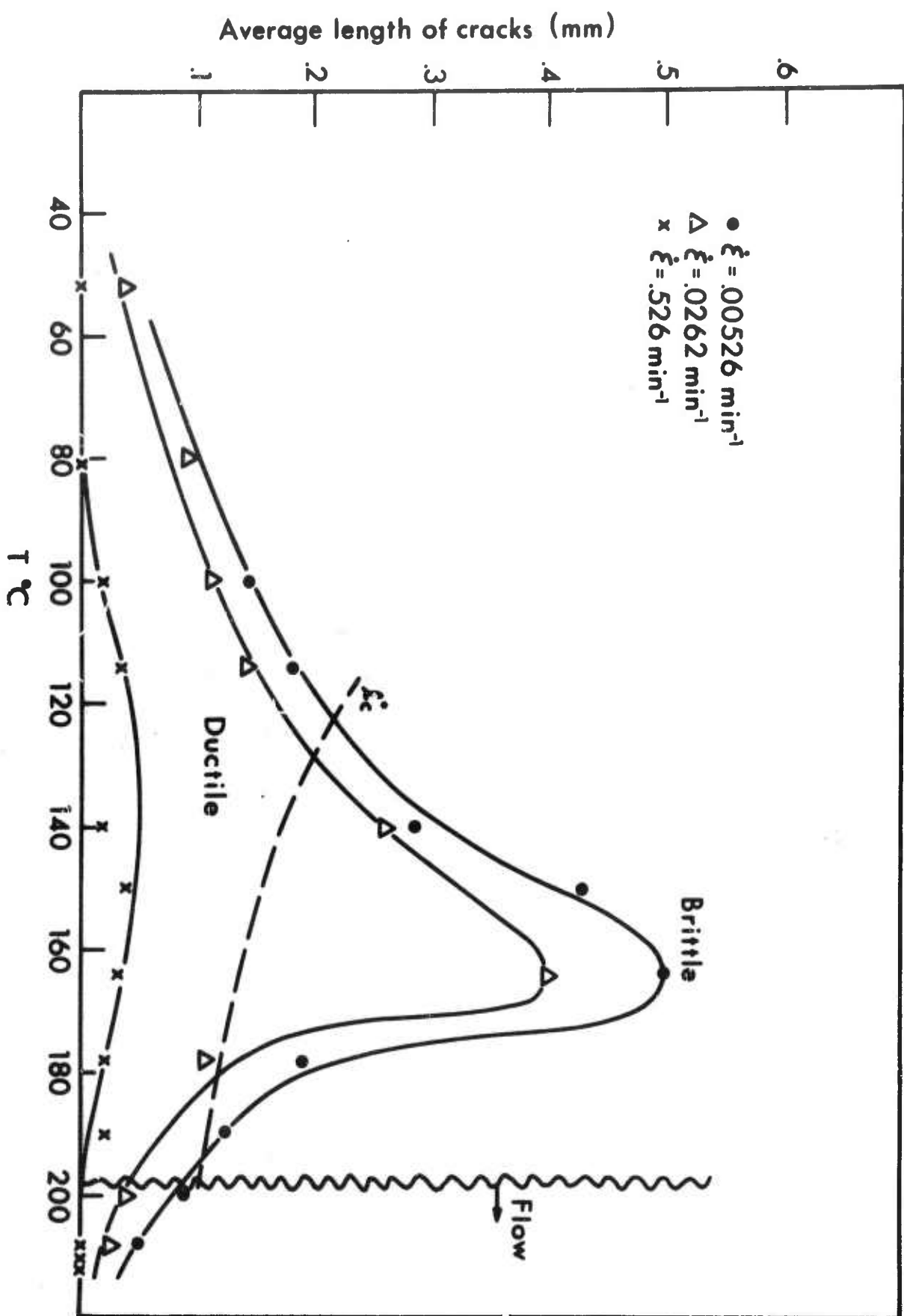


Figure 5. Effect of temperature and strain rate on average defect size.

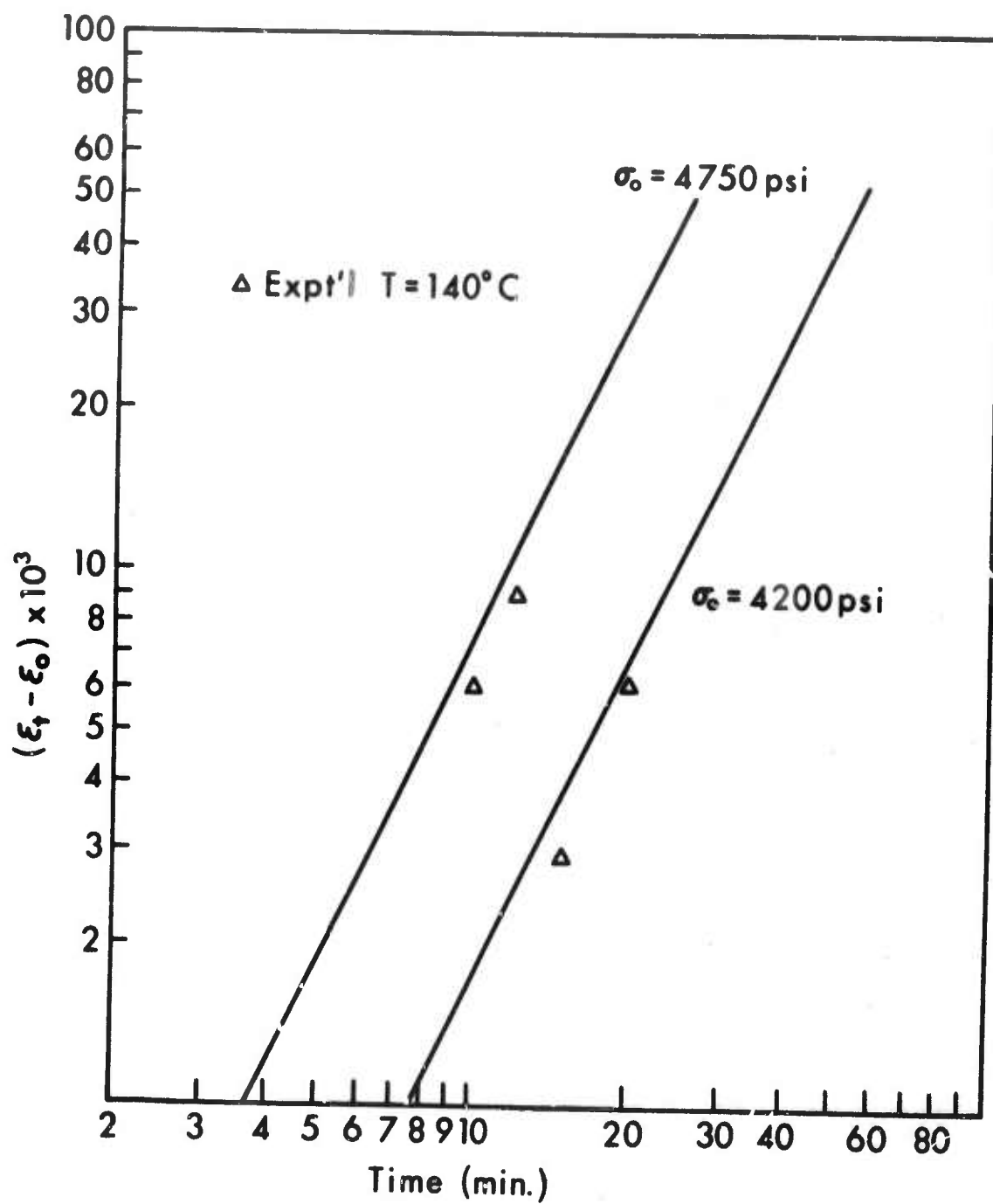


Figure 6. Non-recoverable deformation in creep as a function of time.

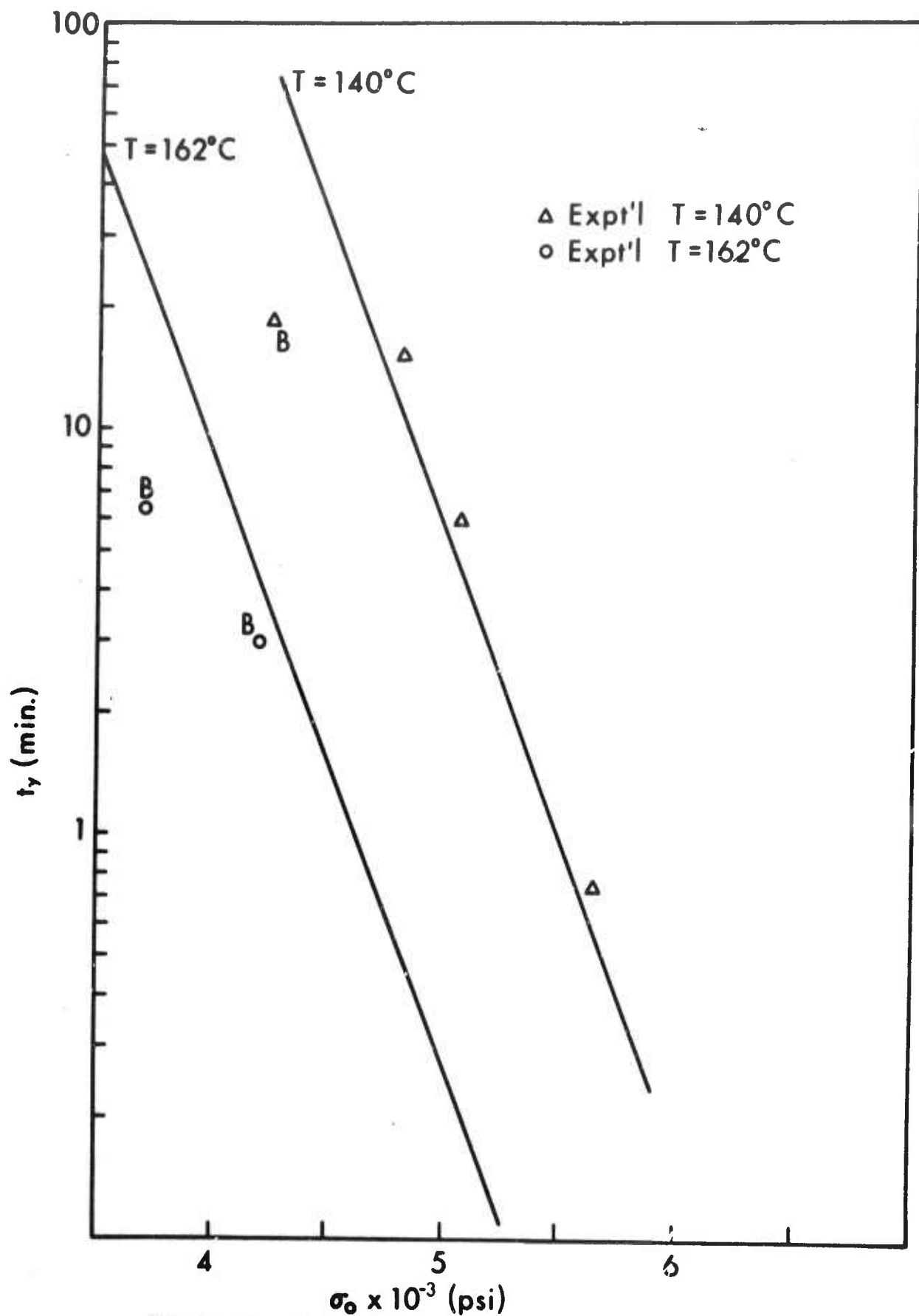


Figure 7. Time to yield under constant load.

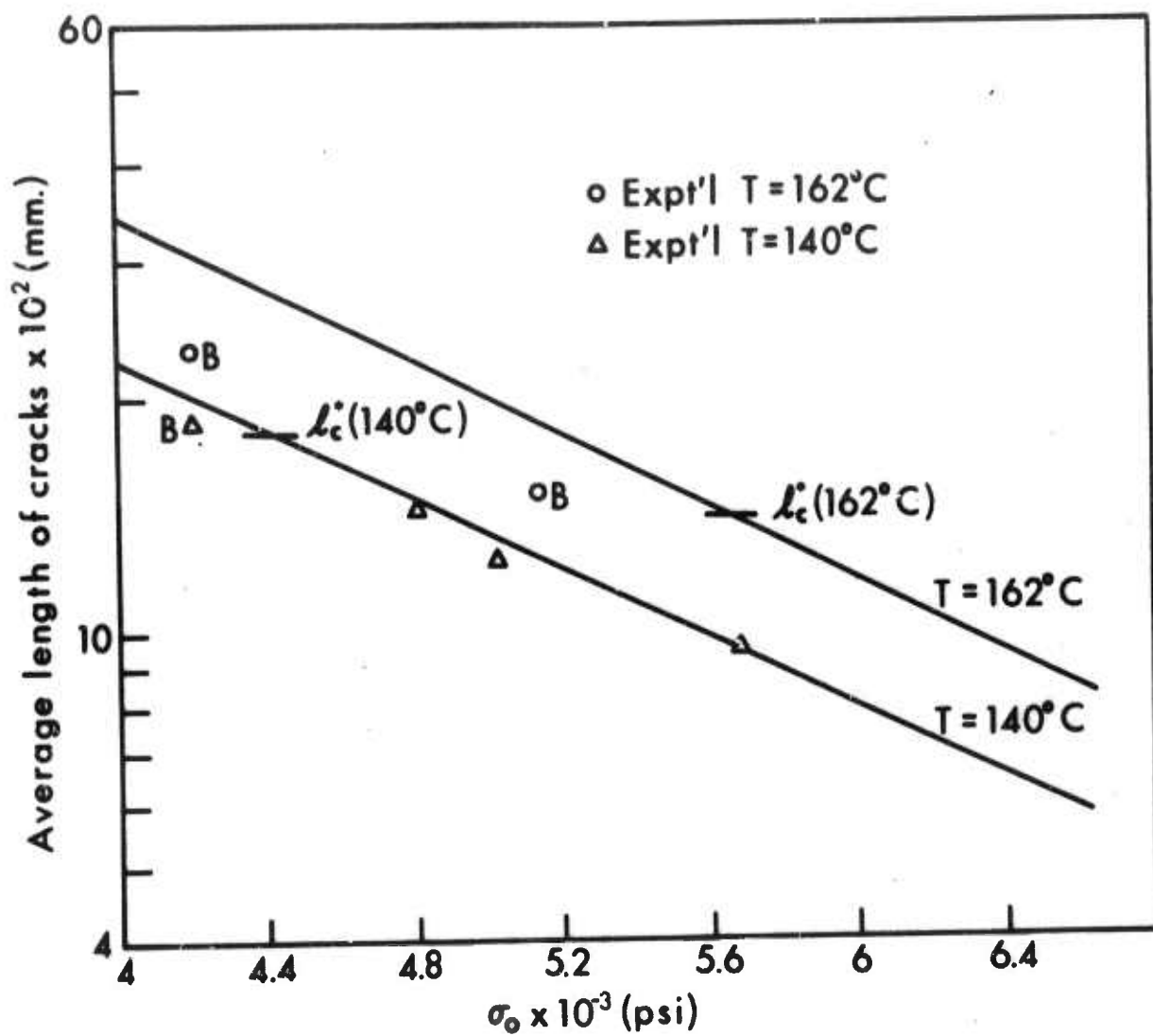


Figure 8. The effect of creep stress on the average defect size.



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13. ABSTRACT			
<p>→ A theory for predicting the stress-strain characteristics of polymeric solids is developed in terms of a description of microdefect formation. The process of irreversible change in these solids is assumed to be a combination of nucleation of submicroscopic defects at stress inhomogeneities and their subsequent growth to macroscopic dimensions. Straining results in the simultaneous generation of free volume and macrodefects so that catastrophic failure can occur through either a general yielding of the material or by brittle fracture.</p> <p>It is assumed that nucleation of sub-microscopic defects is an activated process and that defect growth is one dimensional and linear. The total strain is expressed as the sum of an elastic recoverable strain and a nonlinear, nonrecoverable strain and expressions are obtained for the stress as a function of time, temperature and loading history. The criterion for yielding is defined in terms of free volume concepts and a criterion for brittle failure is defined in terms of a critical defect size. → The parameters of the resulting model are calculated for polyphenylene oxide polymers based on constant rate of loading experiments and then the general creep behavior, including the time required under constant load for cold flow, is predicted. Experimental data are shown to agree with these predictions.</p>			

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